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THEORY OF MOLECULAR COLLISIONS IN THE PRESENCE OF A LASER FIELD\*

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Abstract

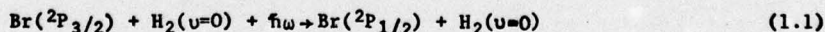
The reaction dynamics and mechanism of energy transfer in a gas-phase molecular collision system can be dramatically affected by an intense, external laser field. A rigorous theoretical treatment must consider explicitly the interaction of the field with the collision dynamics, where the absorption (and emission) of radiation and the molecular collision are viewed as a single process rather than separate, independent processes. The full quantum mechanical formulation yields a set of coupled equations, where the number of equations corresponds to the number of asymptotic channels (a given channel is identified by a field occupation number, vibrational, rotational, nuclear orbital angular momentum and electronic quantum numbers). A semiclassical formulation of the molecular dynamics involves the propagation of classical trajectories and their corresponding actions for nuclear motion on electronic-field potential surfaces, where each electronic-field surface depends on field-free, adiabatic electronic surfaces and radiative coupling (as functions of nuclear coordinates). Transitions between electronic-field surfaces are effected by trajectories propagating through intersection points between the surfaces analytically continued into the complex plane. Numerical results (S-matrix elements) from the quantum and semiclassical approaches have been obtained with model calculations on the process  $\text{Br} + \text{H}_2 + \hbar\omega \rightarrow \text{Br} + \text{H}_2$ .

Introduction

The recent rapid development of laser systems and their use as investigative tools has led to a resurgence of interest in the interaction of matter and radiation. An understanding of this interaction at the microscopic level is necessary if the full potential of laser systems is to be realized. Recent experimental studies on atom-atom collisions have suggested enhancement of inelastic collisional cross sections due to intense optical radiation.<sup>1,2</sup> A theoretical model<sup>3-6</sup> of this phenomenon must treat the collision dynamics of the atoms and their interaction with radiation on the same level of approximation for the following reasons: 1/ in ordinary molecular beams collisions occur in approximately  $10^{-12}$  second, or the cycle of an infrared laser, so the collision and the absorption or emission may not be viewed as separate, distinct processes; and 2/ for intense fields and/or multi-photon processes time-dependent perturbation theory is not valid.

In this paper we focus on atom-atom and atom-diatom collision processes in the presence of a laser field. The theory can describe molecular systems with a large number of electronic states and multi-mode lasers, but for clarity of presentation, we restrict ourselves to two electronic states and a single mode laser. Since our background lies in molecular scattering, we are most interested in the effects of the radiation field on the molecular collision dynamics.

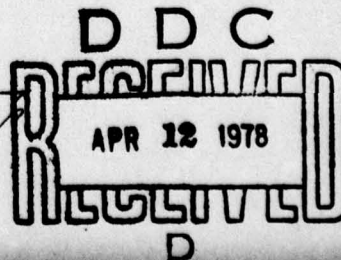
Within the two-(electronic)state approximation both a quantum mechanical theory<sup>7</sup> and a semiclassical theory<sup>8</sup> of molecular scattering in a laser field have been developed, and the essence of these are discussed in the following section. In the third section some numerical results for the process



are discussed. The description of this process involves the construction of electronic-field potential energy surfaces from the original field-free adiabatic surfaces and electric dipole (sometimes magnetic dipole or electric quadrupole) transition matrix elements between electronic states as a function of nuclear coordinates.

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## Theory

A molecular collision process in an electromagnetic field may be described by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(\underline{x}, \underline{q}, t) = \hat{H}(\underline{x}, \underline{q}, t) \Psi(\underline{x}, \underline{q}, t), \quad (2.1)$$

where the total Hamiltonian is:

$$\hat{H}(\underline{x}, \underline{q}, t) = T_{\underline{q}} + H_{el}(\underline{x}, \underline{q}) + \hbar\omega \hat{a} \hat{a}^\dagger + H_{int}(\underline{x}, \underline{q}, t), \quad (2.2)$$

$\underline{x}$  and  $\underline{q}$  represent electronic and nuclear coordinates, respectively, and  $\hat{a}$  ( $\hat{a}^\dagger$ ) are the photon annihilation (creation) operators for the single-mode field of frequency  $\omega$ . The field-free electronic Hamiltonian,  $H_{el}(\underline{x}, \underline{q})$ , contains the electronic kinetic energy as well as the Coulomb potentials among electrons and nuclei.  $H_{int}$  is the Hamiltonian for the interaction between the radiation field and the molecular system and includes all multipole interactions. In practice the dipole approximation is invoked, such that

$$H_{int}(\underline{x}, \underline{q}, t) = \underline{\mu}(\underline{x}, \underline{q}) \cdot \underline{E}(t), \quad (2.3)$$

where  $\underline{E}(t)$  is the electric field, and the transition dipole operator is

$$\underline{\mu} = \sum_j e_j Q_j \quad (2.4)$$

in which  $e_j$  and  $Q_j$  are charges and coordinates of electrons and nuclei.

The total wave function  $\Psi(\underline{x}, \underline{q}, t)$  is expanded in terms of field-free adiabatic surfaces,  $\phi_\ell(\underline{x}, \underline{q})$  as

$$\Psi(\underline{x}, \underline{q}, t) = \sum_{\ell=1}^2 a_\ell(\underline{q}) e^{-i \{E + (\ell-2)\hbar\omega\}t/\hbar} \phi_\ell(\underline{x}, \underline{q}) \quad (2.5)$$

where we have made the two-(electronic)state approximation. Substituting (2.5) into (2.1), multiplying by  $\phi_j(\underline{x}, \underline{q})$  and integrating over  $\underline{x}$  yields a set of coupled equations which may be written in matrix form as

$$(\underline{H} + \underline{Y}) \underline{a} = \underline{E} \underline{a}, \quad (2.6)$$

where:

$$\underline{H} = \begin{pmatrix} T_{\underline{q}} & (T_{\underline{q}})_{11} & 0 \\ 0 & T_{\underline{q}} & (T_{\underline{q}})_{22} \end{pmatrix}, \quad (2.7)$$

$$\underline{Y} = \begin{pmatrix} W_1(\underline{q}) + \hbar\omega & \underline{\mu}_{12} \cdot \underline{E}/2 \\ \underline{\mu}_{21} \cdot \underline{E}/2 & W_2(\underline{q}) \end{pmatrix}, \quad (2.8)$$

$$\underline{a} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (2.9)$$

where:

$$(T_{\underline{q}})_{ij} = \langle \phi_i | T_{\underline{q}} | \phi_j \rangle, \quad (2.10)$$

$$\underline{\mu}_{ij} = \langle \phi_i | \underline{\mu} | \phi_j \rangle, \quad (2.11)$$

$$H_{el}(\underline{x}, \underline{q}) \phi_\ell(\underline{x}, \underline{q}) = W_\ell(\underline{q}) \phi_\ell(\underline{x}, \underline{q}), \quad (2.12)$$

and  $\underline{E}$  is the time-independent amplitude of the electric field in its polarization direction, and the rotating wave approximation has been made. The adiabatic surfaces  $W_1$  and  $W_2$  are strongly coupled through the radiative coupling, so the scattering equations are most appropriately cast in terms of electronic-field surfaces, which are given as

$$E_j = \frac{1}{2} (W_1 + W_2 + \hbar\omega) + \frac{(-1)^j}{2} \left[ (W_2 - W_1 - \hbar\omega)^2 + (\underline{\mu}_{12} \cdot \underline{E}) (\underline{\mu}_{21} \cdot \underline{E}) \right]^{1/2} \quad (2.13)$$

This transformation yields an alternate representation of Eq. (2.6) which may be integrated numerically. The scattering transition amplitude (S-matrix) is then obtained by applying appropriate boundary conditions to the integrated solution matrix.

Semiclassical S-matrix elements for a transition from initial state  $i$  to final state  $f$ , derived from a path



integral representation, are given as<sup>8</sup>

$$S_{fi} = N_{fi} e^{iA_{fi}/\hbar}, \quad (2.14)$$

where  $A_{fi}$  is written in terms of a classical action as

$$A_{fi} = E(t_2 - t_1) + \int_{t_1}^{t_*} dt [T - E_1] + \int_{t_*}^{t_2} dt [T - E_2]. \quad (2.15)$$

$$t_1 \rightarrow -\infty, \quad t_2 \rightarrow +\infty$$

$N_{fi}$  is a normalization factor,  $T$  is the classical nuclear kinetic energy and  $t_*$  is the complex time at which the electronic field surfaces  $E_1$  and  $E_2$  intersect. The summation in Eq.(2.14) is over all classical paths which connect initial state  $i$  to final state  $f$ , switching surfaces at some  $t_*$ . Given the electronic-field surfaces, we first calculate the complex intersection points between them. Then all paths connecting initial and final states are constructed and the action along those paths calculated. Substitution of these into Eqs. (2.14)-(2.15) then yields the  $S$ -matrix elements.

The nonadiabatic coupling between field-free states has been suppressed in Eq. (2.7) and thus the above representation is most appropriate for collision systems which are adiabatic in the absence of a field. Furthermore, the rotating wave approximation introduces conservation of excitation to the field-plus-molecular system. That is, the absorption (emission) of a photon is accompanied by a downward (upward) electronic transition. More rigorous versions of the theory have been developed<sup>7,8</sup> which retain the field-free non-adiabatic coupling and consider the Fock representation of the photon states. This yields a set of coupled equations which can describe multi-photon and multi-surface processes. Either nonadiabatic or radiative coupling may generate transitions between electronic-field surfaces in this representation.

### Calculation

We have previously performed model calculations on halogen +  $H_2$  collisions in the absence of a field<sup>9,10</sup>. An electronic-to-vibrational resonance was observed when the halogen was bromine, due to the near matching of the spin-orbit splitting of bromine and the vibrational spacing of  $H_2$ .

In the present work, we wish to observe the effect of a field upon this resonance, in addition to presenting an example of the preceding formalism. The electric transition dipole of this system has not been calculated and hence is ignored. The electronic-field states thus couple via the magnetic dipole of the bromine atom. This coupling is weak, and in order to produce a noticeable effect, rather large field strengths are required.

We make a two-level approximation for the field as well as the electronic spectra of the system. The field quantum  $\hbar\omega$  is chosen to be slightly greater than  $\lambda$ , the bromine spin-orbit splitting, which is the separation of the electronic states.

$$\hbar\omega = 1.001 \lambda, \quad (3.1)$$

$$\lambda = 0.01678 \text{ Hartree}$$

$$= 0.4566 \text{ eV}. \quad (3.2)$$

The collision energy in the following calculations is .163 eV. In the absence of the field, the probability for an electronic transition without a concomitant vibrational transition is very small. In the presence of a field, the probability of electronic transition increases very rapidly with field strength from threshold at  $5 \times 10^5$  volts/cm to .85 at  $5 \times 10^7$  volts/cm. The electronic-to-vibrational probability falls from .3 to .17 in the same range of field strength. Transition probabilities are also calculated within the vibronic approximation<sup>8,10</sup>. This model requires only two channels whereas the more general treatment employs eight channels altogether. However, the results are surprisingly close, and the semiclassical calculations employing the vibronic model are also in excellent agreement with the full quantum probabilities.

### Discussion and Conclusion

Both a semiclassical model and a coupled-channel quantum mechanical formulation of the field-plus-molecular scattering process have been derived in which the nonadiabatic and radiative coupling are treated equally. Our sample calculation reveals that molecular dynamics are greatly affected by the presence of an intense field, with some cross sections being enhanced while others are damped. Thus a laser field impinging on a scattering region may be tuned to yield products in selected final states.

The electronic-field surfaces, which are characteristic of both the molecular system and the applied laser

# THEORY OF MOLECULAR COLLISIONS IN THE PRESENCE OF A LASER FIELD

field, may support a new spectrum and thus lead to absorptions and emissions not present in the absence of the field. These surfaces may also contain wells able to support metastable states. Preliminary investigations of these effects are underway in our laboratory.

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